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TITLE

ELECTROLUMINESCENT IRIIDIUM COMPOUNDS WITH FLUORINATED
PHENYLPYRIDINES, PHENYLPYRIMIDINES, AND PHENYLQUINOLINES
AND DEVICES MADE WITH SUCH COMPOUNDS

5 BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to electroluminescent complexes of iridium(III) with
fluorinated phenylpyridines, phenylpyrimidines, and phenylquinolines. It also
relates to electronic devices in which the active layer includes an
10 electroluminescent Ir(III) complex.

Description of the Related Art

Organic electronic devices that emit light, such as light-emitting diodes
that make up displays, are present in many different kinds of electronic
equipment. In all such devices, an organic active layer is sandwiched between
15 two electrical contact layers. At least one of the electrical contact layers is light-
transmitting so that light can pass through the electrical contact layer. The
organic active layer emits light through the light-transmitting electrical contact
layer upon application of electricity across the electrical contact layers.

It is well known to use organic electroluminescent compounds as the
20 active component in light-emitting diodes. Simple organic molecules such as
anthracene, thiadiazole derivatives, and coumarin derivatives are known to show
electroluminescence. Semiconductive conjugated polymers have also been used
as electroluminescent components, as has been disclosed in, for example, Friend
et al., U.S. Patent 5,247,190, Heeger et al., U.S. Patent 5,408,109, and Nakano
25 et al., Published European Patent Application 443 861. Complexes of
8-hydroxyquinolate with trivalent metal ions, particularly aluminum, have been
extensively used as electroluminescent components, as has been disclosed in, for
example, Tang et al., U.S. Patent 5,552,678.

Burrows and Thompson have reported that fac-tris(2-phenylpyridine)
30 iridium can be used as the active component in organic light-emitting devices.
(*Appl. Phys. Lett.* 1999, 75, 4.) The performance is maximized when the iridium
compound is present in a host conductive material. Thompson has further
reported devices in which the active layer is poly(N-vinyl carbazole) doped with
fac-tris[2-(4',5'-difluorophenyl)pyridine-C²,N]iridium(III). (Polymer Preprints
35 2000, 41(1), 770.)

However, there is a continuing need for electroluminescent compounds
having improved efficiency.

SUMMARY OF THE INVENTION

The present invention is directed to an iridium compound (generally referred as "Ir(III) compounds") having at least two 2-phenylpyridine ligands in which there is at least one fluorine or fluorinated group on the ligand. The iridium compound has the following First Formula:



where:

$x = 0$ or 1 , $y = 0, 1$ or 2 , and $z = 0$ or 1 , with the proviso that:

$x = 0$ or $y + z = 0$ and

when $y = 2$ then $z = 0$;

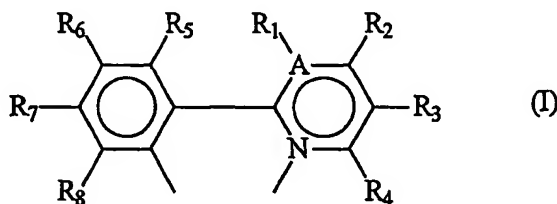
L' = a bidentate ligand or a monodentate ligand, and is not a phenylpyridine, phenylpyrimidine, or phenylquinoline; with the proviso that:

when L' is a monodentate ligand, $y+z = 2$, and

when L' is a bidentate ligand, $z = 0$;

L'' = a monodentate ligand, and is not a phenylpyridine, and phenylpyrimidine, or phenylquinoline; and

L^a , L^b and L^c are alike or different from each other and each of L^a , L^b and L^c has structure (I) below:



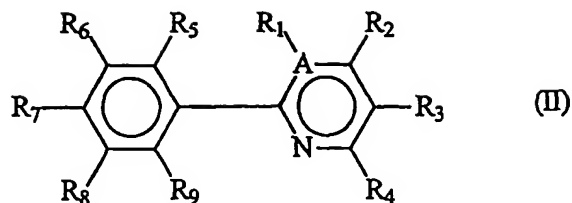
wherein:

adjacent pairs of $\text{R}_1\text{-R}_4$ and $\text{R}_5\text{-R}_8$ can be joined to form a five- or six-membered ring,

at least one of $\text{R}_1\text{-R}_8$ is selected from F , $\text{C}_n\text{F}_{2n+1}$, $\text{OC}_n\text{F}_{2n+1}$, and OCF_2X , where $n = 1\text{-}6$ and $\text{X} = \text{H}$, Cl , or Br , and

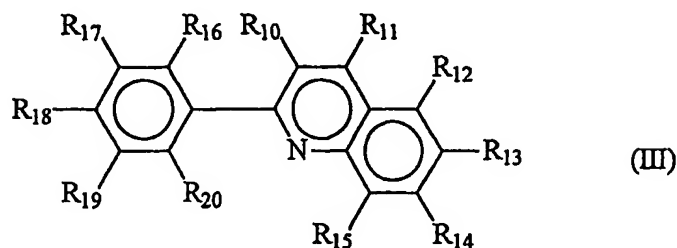
$\text{A} = \text{C}$ or N , provided that when $\text{A} = \text{N}$, there is no R_1 .

In another embodiment, the present invention is directed to substituted 2-phenylpyridine, phenylpyrimidine, and phenylquinoline precursor compounds from which the above Ir(III) compounds are made. The precursor compounds have a structure (II) or (III) below:



where A and R₁-R₈ are as defined in structure (I) above,
and R₉ is H.

5



where:

10

at least one of R₁₀-R₁₉ is selected from F, C_nF_{2n+1},
OC_nF_{2n+1}, and OCF₂X, where n = 1-6 and X = H, Cl, or Br, and
R₂₀ is H.

It is understood that there is free rotation about the phenyl-pyridine,
15 phenyl-pyrimidine and the phenyl-quinoline bonds. However, for the discussion
herein, the compounds will be described in terms of one orientation.

In another embodiment, the present invention is directed to an organic
electronic device having at least one emitting layer comprising the above Ir(III)
compound, or combinations of the above Ir(III) compounds.

20 As used herein, the term "compound" is intended to mean an electrically
uncharged substance made up of molecules that further consist of atoms, wherein
the atoms cannot be separated by physical means. The term "ligand" is intended
to mean a molecule, ion, or atom that is attached to the coordination sphere of a
metallic ion. The term "complex", when used as a noun, is intended to mean a
25 compound having at least one metallic ion and at least one ligand. The term
"group" is intended to mean a part of a compound, such a substituent in an
organic compound or a ligand in a complex. The term "facial" is intended to
mean one isomer of a complex, Ma₃b₃, having octahedral geometry, in which the

three "a" groups are all adjacent, i.e. at the corners of one face of the octahedron. The term "meridional" is intended to mean one isomer of a complex, Ma_3b_3 , having octahedral geometry, in which the three "a" groups occupy three positions such that two are trans to each other. The phrase "adjacent to," when used to refer to layers in a device, does not necessarily mean that one layer is immediately next to another layer. On the other hand, the phrase "adjacent R groups," is used to refer to R groups that are next to each other in a chemical formula (i.e., R groups that are on atoms joined by a bond). The term "photoactive" refers to any material that exhibits electroluminescence and/or photosensitivity.

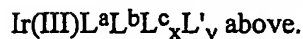
DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic diagram of a light-emitting device (LED).

Figure 2 is a schematic diagram of an LED testing apparatus.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The Ir(III) compounds of the invention have the First Formula



The above Ir(III) compounds are frequently referred to as cyclometalated complexes: Ir(III) compounds having the following Second Formula is also frequently referred to as a bis-cyclometalated complex.:



where:

y, z, L^a , L^b , L' , and L'' are as defined in the First Formula above.

Ir(III) compounds having the following Third Formula is also frequently referred to as a tris-cyclometalated complex.:



where:

L^a , L^b and L^c are as defined in the First Formula described above.

The preferred cyclometalated complexes are neutral and non-ionic, and can be sublimed intact. Thin films of these materials obtained via vacuum deposition exhibit good to excellent electroluminescent properties. Introduction of fluorine substituents into the ligands on the iridium atom increases both the stability and volatility of the complexes. As a result, vacuum deposition can be carried out at lower temperatures and decomposition of the complexes can be avoided. Introduction of fluorine substituents into the ligands can often reduce the non-radiative decay rate and the self-quenching phenomenon in the solid state.

These reductions can lead to enhanced luminescence efficiency. Variation of substituents with electron-donating and electron-withdrawing properties allows for fine-tuning of electroluminescent properties of the compound and hence optimization of the brightness and efficiency in an electroluminescent device.

5 While not wishing to be bound by theory, it is believed that the emission from the iridium compounds is ligand-based, resulting from metal-to-ligand charge transfer. Therefore, compounds that can exhibit electroluminescence include those of compounds of the Second Formula $\text{IrL}^a\text{L}^b\text{L}'_y\text{L}''_z$ above, and the Third Formula $\text{IrL}^a\text{L}^b\text{L}^c$ above, where all L^a , L^b , and L^c in the Third Formula are
10 phenylpyridines, phenylpyrimidines, or phenylquinolines. The R_1 - R_8 groups of structures (I) and (II), and the R_{10} - R_{19} groups of structure (III) above may be chosen from conventional substituents for organic compounds, such as alkyl, alkoxy, halogen, nitro, and cyano groups, as well as fluoro, fluorinated alkyl and fluorinated alkoxy groups. The groups can be partially or fully fluorinated
15 (perfluorinated). Preferred iridium compounds have all R_1 - R_8 and R_{10} - R_{19} substituents selected from fluoro, perfluorinated alkyl ($\text{C}_n\text{F}_{2n+1}$) and perfluorinated alkoxy groups ($\text{OC}_n\text{F}_{2n+1}$), where the perfluorinated alkyl and alkoxy groups have 1-6 carbon atoms, or a group of the formula OCF_2X , where $\text{X} = \text{H}, \text{Cl}, \text{or Br}$.

20 It has been found that the electroluminescent properties of the cyclometalated iridium complexes are poorer when any one or more of the R_1 - R_8 and R_{10} - R_{19} groups is a nitro group. Therefore, it is preferred that none of the R_1 - R_8 and R_{10} - R_{19} groups is a nitro group.

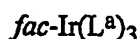
The nitrogen-containing ring can be a pyridine ring, a pyrimidine or a
25 quinoline. It is preferred that at least one fluorinated substituent is on the nitrogen-containing ring; most preferably CF_3 .

Any conventional ligands known to transition metal coordination chemistry is suitable as the L' and L'' ligands. Examples of bidentate ligands include compounds having two coordinating groups, such as ethylenediamine and
30 acetylacetonate, which may be substituted. Examples of monodentate ligands include chloride and nitrate ions and mono-amines. It is preferred that the iridium complex be neutral and sublimable. If a single bidentate ligand is used, it should have a net charge of minus one (-1). If two monodentate ligands are used, they should have a combined net charge of minus one (-1). The bis-cyclometalated
35 complexes can be useful in preparing tris-cyclometalated complexes where the ligands are not all the same.

In a preferred embodiment, the iridium compound has the Third Formula $\text{IrL}^a\text{L}^b\text{L}^c$ as described above.

In a more preferred embodiment, $L^a = L^b = L^c$. These more preferred compounds frequently exhibit a facial geometry, as determined by single crystal X-ray diffraction, in which the nitrogen atoms coordinated to the iridium are trans with respect to carbon atoms coordinated to the iridium. These more preferred

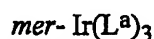
5 compounds have the following Fourth Formula:



(Fourth Formula)

where L^a has structure (I) above.

10 The compounds can also exhibit a meridional geometry in which two of the nitrogen atoms coordinated to the iridium are trans to each other. These compounds have the following Fifth Formula:



(Fifth Formula)

15 where L^a has structure (I) above.

Examples of compounds of the Fourth Formula and Fifth Formula above are given in Table 1 below:

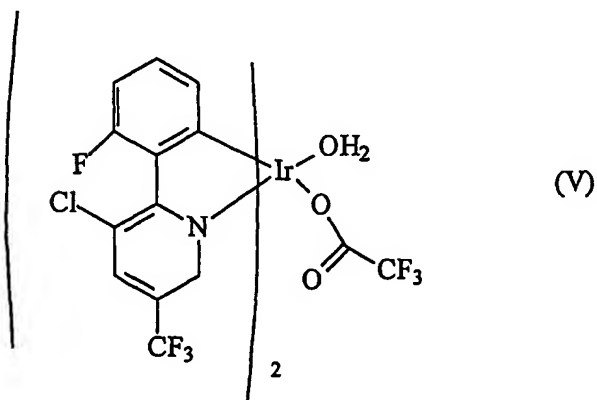
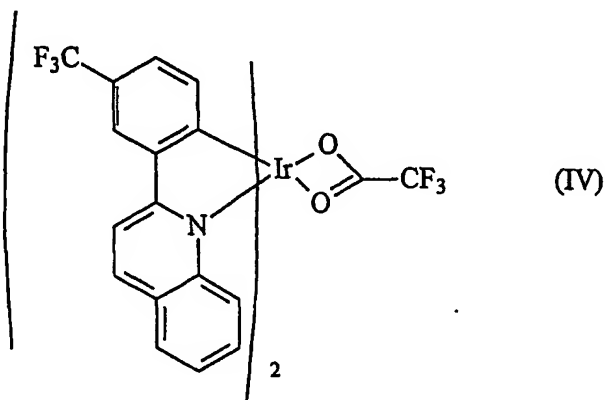
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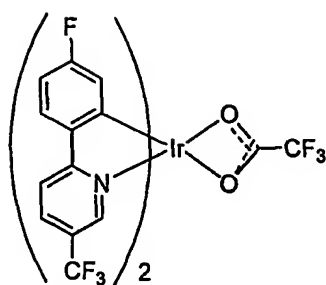
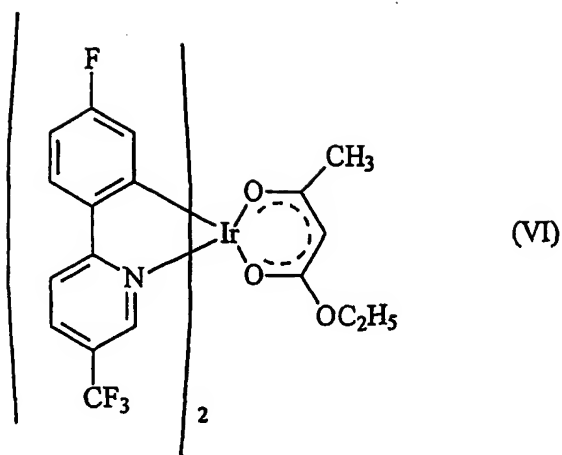
TABLE 1										
Compound	A	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	R ₈	Formula
1-a	C	H	H	CF ₃	H	H	H	H	H	Fourth
1-b	C	H	H	CF ₃	H	H	H	F	H	Fourth
1-c	C	H	H	CF ₃	H	F	H	H	H	Fourth
1-d	C	H	H	H	H	F	H	H	H	Fourth
1-e	C	H	H	CF ₃	H	H	CF ₃	H	H	Fourth
1-f	C	H	H	H	H	H	CF ₃	H	H	Fourth
1-g	C	H	H	H	H	H	H	F	H	Fourth
1-h	C	Cl	H	CF ₃	H	H	H	H	H	Fourth
1-i	C	H	H	CF ₃	H	H	H	OCH ₃	H	Fourth
1-j	C	H	H	CF ₃	H	H	F	H	H	Fourth
1-k	C	H	H	NO ₂	H	H	CF ₃	H	H	Fourth
1-l	C	H	H	CF ₃	H	H	H	OCF ₃	H	Fourth
1-m	N	--	CF ₃	H	H	H	H	F	H	Fourth
1-q	C	H	H	CF ₃	H	H	OCH ₃	H	H	Fourth

TABLE 1										
Compound	A	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	R ₈	Formula
1-r	C	H	<u>OCH₃</u>	H	H	H	H	CF ₃	H	Fourth
1-s	C	H	<u>H</u>	H	H	F	H	F	H	Fourth and Fifth
1-t	C	H	<u>H</u>	CF ₃	H	H	F	H	F	Fifth
1-u	C	H	<u>H</u>	CF ₃	H	F	H	F	H	Fifth
1-v	C	H	H	CF ₃	H	H	H	F	H	Fifth

Examples compounds of the Second Formula $\text{IrL}^a\text{L}^b\text{L}'_y\text{L}''_z$ above include compounds 1-n, 1-o, 1-p, 1-w and 1-x, respectively having structure (IV), (V), (VI), (IX) and (X) below:

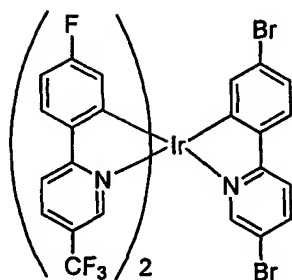
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(IX)



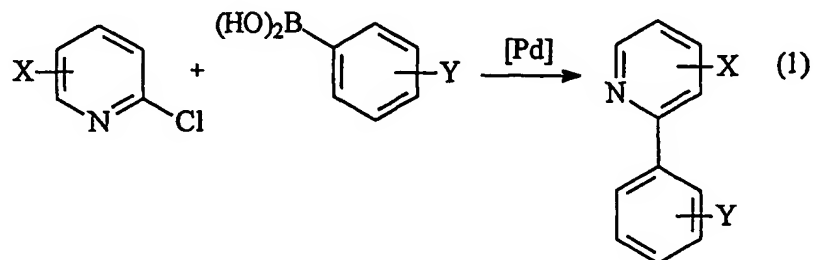
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(X)

The iridium complexes of the Third Formula $\text{IrL}^{\text{a}}\text{L}^{\text{b}}\text{L}^{\text{c}}$ above are generally prepared from the appropriate substituted 2-phenylpyridine, phenylpyrimidine, or

phenylquinoline. The substituted 2-phenylpyridines, phenylpyrimidines, and phenylquinolines, as shown in Structure (II) above, are prepared, in good to excellent yield, using the Suzuki coupling of the substituted 2-chloropyridine, 2-chloropyrimidine or 2-chloroquinoline with arylboronic acid as described in

- 5 O. Lohse, P.Thevenin, E. Waldvogel *Synlett*, 1999, 45-48. This reaction is illustrated for the pyridine derivative, where X and Y represent substituents, in Equation (1) below:



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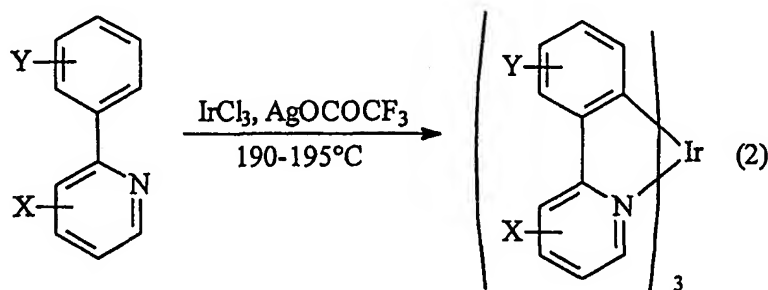
Examples of 2-phenylpyridine and 2-phenylpyrimidine compounds, having structure (II) above, are given in Table 2 below:

TABLE 2										
Compound	A	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	R ₈	R ₉
2-a	C	H	H	CF ₃	H	F	H	H	H	H
2-b	C	H	H	CF ₃	H	H	CF ₃	H	H	H
2-c	C	H	H	NO ₂	H	H	CF ₃	H	H	H
2-d	C	H	H	CF ₃	H	H	F	H	H	H
2-e	C	H	H	CF ₃	H	H	H	CH ₃ O	H	H
2-f	C	Cl	H	CF ₃	H	H	H	H	H	H
2-g	C	H	H	H	CH ₃	H	H	F	H	H
2-h	N	—	H	H	H	H	H	F	H	H
2-i	C	H	H	CF ₃	H	H	H	CF ₃ O	H	H
2-j	N	—	CF ₃	H	H	F	H	H	H	H
2-k	C	H	H	CF ₃	H	H	H	F	H	H
2-l	C	CF ₃	H	H	H	H	H	H	H	H
2-m	C	Cl	H	CF ₃	H	H	H	F	H	H
2-n	C	CF ₃	H	H	H	H	H	F	H	H
2-o	C	CF ₃	H	H	H	H	H	CH ₃ O	H	H
2-p	C	Cl	H	CF ₃	H	H	H	CH ₃ O	H	H

TABLE 2										
Compound	A	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	R ₈	R ₉
2-q	N	—	CF ₃	H	H	H	H	F	H	H
2-r	C	Cl	H	CF ₃	H	H	H	H	H	F
2-s	C	H	H	CF ₃	H	H	H	H	H	H
2-t	C	Cl	H	H	H	F	H	H	H	H
2-v	C	H	H	CF ₃	H	H	CH ₃ O	H	H	H
2-w	C	H	CH ₃ O	H	H	H	H	CF ₃	H	H
2-x	C	H	H	H	H	H	F	F	H	H
2-y	C	H	H	CF ₃	H	H	F	H	F	H
2-z	C	H	H	CF ₃	H	F	H	F	H	H
2-aa	C	H	H	Br	H	H	H	Br	H	H

One example of a substituted 2-phenylquinoline compound, having structure (III) above, is compound 2-u, which has R₁₇ = CF₃ and R₁₀-R₁₆ and R₁₈-R₂₀ = H.

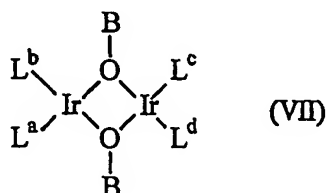
- 5 The 2-phenylpyridines, pyrimidines, and quinolines thus prepared are used for the synthesis of the cyclometalated iridium complexes. A convenient one-step method has been developed employing commercially available iridium trichloride hydrate and silver trifluoroacetate. The reactions are generally carried out with an excess of 2-phenylpyridine, pyrimidine, or quinoline, without a solvent, in the
- 10 presence of 3 equivalents of AgOCOCF₃. This reaction is illustrated for a 2-phenylpyridine in Equation (2) below:



- 15 The tris-cyclometalated iridium complexes were isolated, purified, and fully characterized by elemental analysis, ¹H and ¹⁹F NMR spectral data, and, for compounds 1-b, 1-c, and 1-e, single crystal X-ray diffraction. In some cases, mixtures of isomers are obtained. Often the mixture can be used without isolating the individual isomers.

The iridium complexes having the Second Formula $\text{IrL}^a\text{L}^b\text{L}'^y\text{L}''^z$ above, may, in some cases, be isolated from the reaction mixture using the same synthetic procedures as preparing those having Third Formula $\text{IrL}^a\text{L}^b\text{L}^c$ above.

The complexes can also be prepared by first preparing an intermediate iridium dimer having structure VII below:



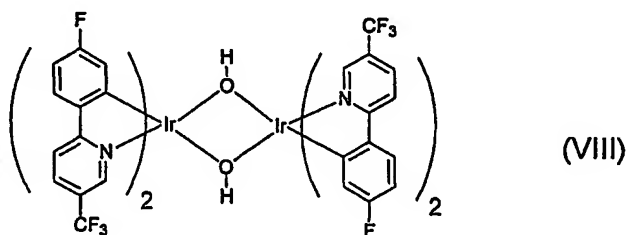
wherein:

$\text{B} = \text{H}, \text{CH}_3, \text{ or } \text{C}_2\text{H}_5$, and

$\text{L}^a, \text{L}^b, \text{L}^c$, and L^d can be the same or different from each other and each of $\text{L}^a, \text{L}^b, \text{L}^c$, and L^d has structure (I) above.

The iridium dimers can generally be prepared by first reacting iridium trichloride hydrate with the 2-phenylpyridine, phenylpyrimidine or phenylquinoline, and adding NaOB.

One particularly useful iridium dimer is the hydroxo iridium dimer, having structure VIII below:



This intermediate can be used to prepare compound 1-p by the addition of ethyl acetoacetate.

Electronic Device

The present invention also relates to an electronic device comprising at least one photoactive layer positioned between two electrical contact layers, wherein the at least one layer of the device includes the iridium complex of the invention. Devices frequently have additional hole transport and electron transport layers. A typical structure is shown in Figure 1. The device 100 has an anode layer 110 and a cathode layer 150. Adjacent to the anode is a layer 120

comprising hole transport material. Adjacent to the cathode is a layer 140 comprising an electron transport material. Between the hole transport layer and the electron transport layer is the photoactive layer 130.

Depending upon the application of the device 100, the photoactive layer 130 can be a light-emitting layer that is activated by an applied voltage (such as in a light-emitting diode or light-emitting electrochemical cell), a layer of material that responds to radiant energy and generates a signal with or without an applied bias voltage (such as in a photodetector). Examples of photodetectors include photoconductive cells, photoresistors, photoswitches, phototransistors, and phototubes, and photovoltaic cells, as these terms are describe in Markus, John, *Electronics and Nucleonics Dictionary*, 470 and 476 (McGraw-Hill, Inc. 1966).

The iridium compounds of the invention are particularly useful as the photoactive material in layer 130, or as electron transport material in layer 140. Preferably the iridium complexes of the invention are used as the light-emitting material in diodes. It has been found that in these applications, the fluorinated compounds of the invention do not need to be in a solid matrix diluent in order to be effective. A layer that is greater than 20% by weight iridium compound, based on the total weight of the layer, up to 100% iridium compound, can be used as the emitting layer. This is in contrast to the non-fluorinated iridium compound, tris(2-phenylpyridine) iridium (III), which was found to achieve maximum efficiency when present in an amount of only 6-8% by weight in the emitting layer. This was necessary to reduce the self-quenching effect. Additional materials can be present in the emitting layer with the iridium compound. For example, a fluorescent dye may be present to alter the color of emission. A diluent may also be added. The diluent can be a polymeric material, such as poly(N-vinyl carbazole) and polysilane. It can also be a small molecule, such as 4,4'-N,N'-dicarbazole biphenyl or tertiary aromatic amines. When a diluent is used, the iridium compound is generally present in a small amount, usually less than 20% by weight, preferably less than 10% by weight, based on the total weight of the layer.

In some cases the iridium complexes may be present in more than one isomeric form, or mixtures of different complexes may be present. It will be understood that in the above discussion of OLEDs, the term "the iridium compound" is intended to encompass mixtures of compounds and/or isomers.

To achieve a high efficiency LED, the HOMO (highest occupied molecular orbital) of the hole transport material should align with the work function of the anode, the LUMO (lowest un-occupied molecular orbital) of the electron transport material should align with the work function of the cathode.

Chemical compatibility and sublimation temp of the materials are also important considerations in selecting the electron and hole transport materials.

The other layers in the OLED can be made of any materials which are known to be useful in such layers. The anode 110, is an electrode that is particularly efficient for injecting positive charge carriers. It can be made of, for example materials containing a metal, mixed metal, alloy, metal oxide or mixed-metal oxide, or it can be a conducting polymer. Suitable metals include the Group 11 metals, the metals in Groups 4, 5, and 6, and the Group 8-10 transition metals. If the anode is to be light-transmitting, mixed-metal oxides of Groups 12, 13 and 14 metals, such as indium-tin-oxide, are generally used. The IUPAC numbering system is used throughout, where the groups from the Periodic Table are numbered from left to right as 1-18 (CRC Handbook of Chemistry and Physics, 81st Edition, 2000). The anode 110 may also comprise an organic material such as polyaniline as described in "Flexible light-emitting diodes made from soluble conducting polymer," *Nature* vol. 357, pp 477-479 (11 June 1992). At least one of the anode and cathode should be at least partially transparent to allow the generated light to be observed.

Examples of hole transport materials for layer 120 have been summarized for example, in Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, Vol. 18, p. 837-860, 1996, by Y. Wang. Both hole transporting molecules and polymers can be used. Commonly used hole transporting molecules are: N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD), 1,1-bis[(di-4-tolylamino) phenyl]cyclohexane (TAPC), N,N'-bis(4-methylphenyl)-N,N'-bis(4-ethylphenyl)-[1,1'-(3,3'-dimethyl)biphenyl]-4,4'-diamine (ETPD), tetrakis-(3-methylphenyl)-N,N,N',N'-2,5-phenylenediamine (PDA), a-phenyl-4-N,N-diphenylaminostyrene (TPS), p-(diethylamino)-benzaldehyde diphenylhydrazone (DEH), triphenylamine (TPA), bis[4-(N,N-diethylamino)-2-methylphenyl](4-methylphenyl)methane (MPMP), 1-phenyl-3-[p-(diethylamino)styryl]-5-[p-(diethylamino)phenyl] pyrazoline (PPR or DEASP), 1,2-trans-bis(9H-carbazol-9-yl)cyclobutane (DCZB), N,N,N',N'-tetrakis(4-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TTB), and porphyrinic compounds, such as copper phthalocyanine. Commonly used hole transporting polymers are polyvinylcarbazole, (phenylmethyl)polysilane, and polyaniline. It is also possible to obtain hole transporting polymers by doping hole transporting molecules such as those mentioned above into polymers such as polystyrene and polycarbonate.

Examples of electron transport materials for layer 140 include metal chelated oxinoid compounds, such as tris(8-hydroxyquinolato)aluminum (Alq₃); phenanthroline-based compounds, such as 2,9-dimethyl-4,7-diphenyl-1,10-

phenanthroline (DDPA) or 4,7-diphenyl-1,10-phenanthroline (DPA), and azole compounds such as 2-(4-biphenyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole (PBD) and 3-(4-biphenyl)-4-phenyl-5-(4-t-butylphenyl)-1,2,4-triazole (TAZ). Layer 140 can function both to facilitate electron transport, and also serve as a buffer layer or confinement layer to prevent quenching of the exciton at layer interfaces. Preferably, this layer promotes electron mobility and reduces exciton quenching.

The cathode 150, is an electrode that is particularly efficient for injecting electrons or negative charge carriers. The cathode can be any metal or nonmetal having a lower work function than the anode. Materials for the cathode can be selected from alkali metals of Group 1 (e.g., Li, Cs), the Group 2 (alkaline earth) metals, the Group 12 metals, including the rare earth elements and lanthanides, and the actinides. Materials such as aluminum, indium, calcium, barium, samarium and magnesium, as well as combinations, can be used. Li-containing organometallic compounds can also be deposited between the organic layer and the cathode layer to lower the operating voltage.

It is known to have other layers in organic electronic devices. For example, there can be a layer (not shown) between the conductive polymer layer 120 and the active layer 130 to facilitate positive charge transport and/or band-gap matching of the layers, or to function as a protective layer. Similarly, there can be additional layers (not shown) between the active layer 130 and the cathode layer 150 to facilitate negative charge transport and/or band-gap matching between the layers, or to function as a protective layer. Layers that are known in the art can be used. In addition, any of the above-described layers can be made of two or more layers. Alternatively, some or all of inorganic anode layer 110, the conductive polymer layer 120, the active layer 130, and cathode layer 150, may be surface treated to increase charge carrier transport efficiency. The choice of materials for each of the component layers is preferably determined by balancing the goals of providing a device with high device efficiency.

It is understood that each functional layer may be made up of more than one layer.

The device can be prepared by sequentially vapor depositing the individual layers on a suitable substrate. Substrates such as glass and polymeric films can be used. Conventional vapor deposition techniques can be used, such as thermal evaporation, chemical vapor deposition, and the like. Alternatively, the organic layers can be coated from solutions or dispersions in suitable solvents, using any conventional coating technique. In general, the different layers will have the following range of thicknesses: anode 110, 500-5000Å, preferably 1000-2000Å; hole transport layer 120, 50-1000Å, preferably 200-800Å; light-emitting layer

130, 10-1000 Å, preferably 100-800Å; electron transport layer 140, 50-1000Å, preferably 200-800Å; cathode 150, 200-10000Å, preferably 300-5000Å. The location of the electron-hole recombination zone in the device, and thus the emission spectrum of the device, can be affected by the relative thickness of each layer. Thus the thickness of the electron-transport layer should be chosen so that the electron-hole recombination zone is in the light-emitting layer. The desired ratio of layer thicknesses will depend on the exact nature of the materials used.

It is understood that the efficiency of devices made with the iridium compounds of the invention, can be further improved by optimizing the other layers in the device. For example, more efficient cathodes such as Ca, Ba or LiF can be used. Shaped substrates and novel hole transport materials that result in a reduction in operating voltage or increase quantum efficiency are also applicable. Additional layers can also be added to tailor the energy levels of the various layers and facilitate electroluminescence.

The iridium complexes of the invention often are phosphorescent and photoluminescent and may be useful in applications other than OLEDs. For example, organometallic complexes of iridium have been used as oxygen sensitive indicators, as phosphorescent indicators in bioassays, and as catalysts. The bis cyclometalated complexes can be used to synthesize tris cyclometalated complexes where the third ligand is the same or different.

EXAMPLES

The following examples illustrate certain features and advantages of the present invention. They are intended to be illustrative of the invention, but not limiting. All percentages are by weight, unless otherwise indicated.

EXAMPLE 1

This example illustrates the preparation of the 2-phenylpyridines and 2-phenylpyrimidines which are used to form the iridium compounds.

The general procedure used was described in O. Lohse, P. Thevenin, E. Waldvogel *Synlett*, 1999, 45-48. In a typical experiment, a mixture of 200 ml of degassed water, 20 g of potassium carbonate, 150 ml of 1,2-dimethoxyethane, 0.5 g of Pd(PPh₃)₄, 0.05 mol of a substituted 2-chloropyridine (quinoline or pyrimidine) and 0.05 mol of a substituted phenylboronic acid was refluxed (80-90°C) for 16-30 h. The resulting reaction mixture was diluted with 300 ml of water and extracted with CH₂Cl₂ (2 x 100 ml). The combined organic layers were dried over MgSO₄, and the solvent removed by vacuum. The liquid products were purified by fractional vacuum distillation. The solid materials were recrystallized from hexane. The typical purity of isolated materials was >98%.

The starting materials, yields, melting and boiling points of the new materials are given in Table 3. NMR data and analytical data are given in Table 4.

TABLE 3

Preparation of 2-Phenyl Pyridines, Phenylpyrimidines and Phenylquinolines

Compound	Yield in %	B.p./ mm Hg (m.p.) in °C
2-s	70	---
2-a	72	---
2-b	48	---
2-u	75	(76-78)
2-c	41	(95-96)
2-d	38	(39-40)
2-e	55	74.5/0.1
2-g	86	71-73/0.07
2-t	65	77-78/0.046
2-k	50	(38-40)
2-m	80	72-73/0.01
2-f	22	52-53/0.12
2-v	63	95-96/13
2-w	72	
2-x	35	61-62/0.095
2-y	62	(68-70)
2-z	42	66-67/0.06 (58-60)
2-aa	60	

TABLE 4
Properties of 2-Phenyl Pyridines, Phenylpyrimidines and Phenylquinolines

Compound	¹ H NMR	¹⁹ F NMR	Analysis %, found (calc.) or MS (M ⁺)
2-s	7.48(3H), 7.70(1H), 7.83(1H), 7.90(2H), 8.75(1H)	-62.68	C, 64.50 (64.57) H, 3.49 (3.59) N, 6.07 (6.28)
2-a	7.19(1H), 7.30(1H), 7.43(1H), 7.98(2H), 8.07 (1H) 9.00(1H)	-60.82 (3F,s), -116.96 (1F, m)	C, 59.56 (59.75) H, 3.19 (2.90) N, 5.52 (5.81)
2-b	7.58(1H), 7.66(1H), 7.88(1H), 8.03(1H), 8.23(1H), 8.35 (1H) 8.99(1H)	-62.75 (3F,s), -63.10 (3F, s)	C, 53.68 (53.60) H, 2.61 (2.40) N, 4.53 (4.81)
2-u	7.55(1H), 7.63(1H), 7.75(2H), 7.89(2H), 8.28(2H), 8.38(1H), 8.50 (1H)	-62.89 (s)	C, 69.17 (70.33) H, 3.79 (3.66) N, 4.88 (5.12)
2-c	7.53(1H), 7.64(1H), 7.90(1H), 8.18(1H), 8.30(1H), 8.53(1H), 9.43(1H)	-62.14 (s)	C, 53.83 (53.73) H, 2.89 (2.61) N, 9.99 (10.44)
2-d	7.06(1H), 7.48(1H), 7.81(3H), 8.01(1H), 8.95(1H),	-62.78 (3F, s), -112.61 (1F,m)	C, 59.73 (59.75) H, 2.86 (2.90) N, 5.70 (5.81)

TABLE 4
(continued)

Compound	¹ H NMR	¹⁹ F NMR	Analysis %, found (calc.) or MS (M ⁺)
2-e	3.80(3H), 6.93(2H), 7.68(1H), 7.85(1H), 7.96(2H), 8.82(1H),	-62.63 (s)	C, 61.66 (61.90) H, 3.95 (4.04) N, 5.53 (5.38)
2-g	2.70(3H), 7.10(3H), 7.48(1H), 7.60(1H), 8.05(2H),	-114.03 (m)	C, 76.56 (77.00) H, 5.12 (5.30) N, 5.43 (7.50)
2-t	7.10(2H), 7.35(2H), 7.96(1H), 8.78(1H),	-62.73 (3F, s) -113.67 (1F, m)	C, 50.51 (52.17) H, 1.97 (2.17) N, 5.09 (5.07)
2-k	7.08(2H), 7.62(1H), 7.90(3H), 8.80(1H),	-62.75 (3F, s) -111.49 (m)	C, 60.39 (59.75), H, 3.38 (2.90), N, 5.53 (5.51)
2-m	7.10(2H), 7.80(2H), 8.00(1H), 8.75(1H),	-62.63 (3F, s) -111.24 (m)	C, 52.13 (52.17) H, 2.16 (2.17) N, 4.85 (5.07)
2-f	7.55(3H), 7.77(2H), 8.06(1H), 8.87(1H)	-62.57(s)	257(M ⁺ , C ₁₂ H ₇ F ₃ ClN ⁺), 222(M-Cl)
2-v	3.8(3H), 6.95(1H), 7.30(1H), 7.50(1H), 7.58(1H), 7.75(1H), 7.90(1H), 8.87(1H)	-62.70 ppm	C, 61.66 (61.37), H, 3.98 (3.67), N, 5.53 (5.48)

TABLE 4
(continued)

Compound	¹ H NMR	¹⁹ F NMR	Analysis %, found (calc.) or MS (M ⁺)
2-w	8.54 (1H, d), 8.21 (2H, d), 7.70 (2H, d), 7.24 (1H, s), 6.82 (1H, dd), 3.91 (3H, s)	-63.08 (3F, s)	
2-x	6.9 (2H, m), 7.18 (2H, m), 7.68 (2H, m), 7.95 (1H, m), 8.65 (1H, m);	-109.70 (1F, m), -113.35 (1F, m).	
2-y	6.94 (1H), 7.62 (2H), 7.82 (1H), 8.03 (1H), 8.96 (1H);	-62.72 (3F, s), -109.11 (2F, m)	
2-z	6.85 (1H), 6.93 (1H), 7.80, 7.90, 8.05 (3H), 8.89 (1H);	-62.80 (3F, s), -107.65 (1F, m), -112.45 (1F, m).	
2-aa	7.70 (3H, m), 7.85 (3H, m), 7.80, 7.90, 8.85 (1H, m).		

EXAMPLE 2

This example illustrates the preparation of iridium compounds of the Fourth Formula *fac*-Ir(L^a)₃ above.

- 5 In a typical experiment, a mixture of IrCl₃·nH₂O (53-55% Ir), AgOCOCF₃ (3.1 equivalents per Ir), 2-arylpyridine (excess), and (optionally) a small amount of water was vigorously stirred under N₂ at 180-195°C (oil bath) for 2-8 hours. The resulting mixture was thoroughly extracted with CH₂Cl₂ until the extracts were colorless. The extracts were filtered through a silica column to produce a
- 10 clear yellow solution. Evaporation of this solution gave a residue which was treated with methanol to produce colored crystalline tris-cyclometalated Ir complexes. The complexes were separated by filtration, washed with methanol, dried under vacuum, and (optionally) purified by crystallization, vacuum

sublimation, or Soxhlet extraction. Yields: 10-82%. All materials were characterized by NMR spectroscopic data and elemental analysis, and the results are given in Table 5 below. Single-crystal X-ray structures were obtained for three complexes of the series.

5 Compound 1-b

A mixture of $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$ (54% Ir; 508 mg), 2-(4-fluorophenyl)-5-trifluoromethylpyridine, compound kk (2.20 g), AgOCOCF_3 (1.01 g), and water (1 mL) was vigorously stirred under a flow of N_2 as the temperature was slowly (30 min) brought up to 185°C (oil bath). After 2 hours at 185-190°C the mixture
10 solidified. The mixture was cooled down to room temperature. The solids were extracted with dichloromethane until the extracts decolorized. The combined dichloromethane solutions were filtered through a short silica column and evaporated. After methanol (50 mL) was added to the residue the flask was kept at -10°C overnight. The yellow precipitate of the tris-cyclometalated complex,
15 compound b, was separated, washed with methanol, and dried under vacuum. Yield: 1.07 g (82%). X-Ray quality crystals of the complex were obtained by slowly cooling its warm solution in 1,2-dichloroethane.

Compound 1-e

A mixture of $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$ (54% Ir; 504 mg), 2-(3-trifluoromethylphenyl)-5-trifluoromethylpyridine, compound bb (1.60 g), and AgOCOCF_3 (1.01 g) was
20 vigorously stirred under a flow of N_2 as the temperature was slowly (15 min) brought up to 192°C (oil bath). After 6 hours at 190-195°C the mixture solidified. The mixture was cooled down to room temperature. The solids were placed on a silica column which was then washed with a large quantity of dichloromethane.
25 The residue after evaporation of the filtrate was treated with methanol to produce yellow solid. The solid was collected and purified by extraction with dichloromethane in a 25-mL micro-Soxhlet extractor. The yellow precipitate of the tris-cyclometalated complex, compound e, was separated, washed with methanol, and dried under vacuum. Yield: 0.59 g (39%). X-Ray quality crystals
30 of the complex were obtained from hot 1,2-dichloroethane.

Compound 1-d

A mixture of $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$ (54% Ir; 508 mg), 2-(2-fluorophenyl)-5-trifluoromethylpyridine, compound aa (1.53 g), and AgOCOCF_3 (1.01 g) was
35 vigorously stirred under a flow of N_2 at 190-195°C (oil bath) for 6 h 15 min. The mixture was cooled down to room temperature and then extracted with hot 1,2-dichloroethane. The extracts were filtered through a short silica column and evaporated. Treatment of the residue with methanol (20 mL) resulted in precipitation of the desired product, compound d, which was separated by

filtration, washed with methanol, and dried under vacuum. Yield: 0.63 g (49%). X-Ray quality crystals of the complex were obtained from dichloromethane / methanol.

Compound 1-i

- 5 A mixture of $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$ (54% Ir; 503 mg), 2-(4-trifluoromethoxyphenyl)-5-trifluoromethylpyridine, compound ee (2.00 g), and AgOCOCF_3 (1.10 g) was vigorously stirred under a flow of N_2 at 190-195°C (oil bath) for 2 h 45 min. The mixture was cooled down to room temperature and then extracted with dichloromethane. The extracts were filtered through a short silica column and
- 10 evaporated. Treatment of the residue with methanol (20 mL) resulted in precipitation of the desired product, compound i, which was separated by filtration, washed with methanol, and dried under vacuum. The yield was 0.86 g. Additionally, 0.27 g of the complex was obtained by evaporating the mother liquor and adding petroleum ether to the residue. Overall yield: 1.13 g (72%).

15 Compound 1-q

- A mixture of $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$ (54% Ir; 530 mg), 2-(3-methoxyphenyl)-5-trifluoromethylpyridine (2.50 g), AgOCOCF_3 (1.12 g), and water (1 mL) was vigorously stirred under a flow of N_2 as the temperature was slowly (30 min) brought up to 185 °C (oil bath). After 1 hour at 185 °C the mixture solidified.
- 20 The mixture was cooled down to room temperature. The solids were extracted with dichloromethane until the extracts decolorized. The combined dichloromethane solutions were filtered through a short silica column and evaporated. The residue was washed with hexanes and then recrystallized from 1,2-dichloroethane - hexanes (twice). Yield: 0.30 g. ^{19}F NMR (CD_2Cl_2 , 20 °C),
- 25 δ : -63 (s). ^1H NMR (CD_2Cl_2 , 20 °C), δ : 8.1 (1H), 7.9 (1H), 7.8 (1H), 7.4 (1H), 6.6 (2H), 4.8 (3H). X-Ray quality crystals of the complex (1,2-dichloroethane, hexane solvate) were obtained from 1,2-dichloroethane - hexanes. This facial complex was orange-photoluminescent.

- Compounds 1-a, 1-c, 1-f through 1-h, 1-j through 1-m, and 1-r were
- 30 similarly prepared. In the preparation of compound 1-j, a mixture of isomers was obtained with the fluorine in either the R_6 or R_8 position.

TABLE 5		
Compound	Analysis (calcd (found))	NMR (CD ₂ Cl ₂ , 25°C)
1-a	C: 50.3 (50.1) H: 2.5 (2.7) N: 4.9 (4.9) Cl: 0.0 (0.2)	¹ H: 6.8 (1H), 6.9 (1H), 7.0 (1H), 7.8 (2H), 7.95 (1H), 8.1 (1H) ¹⁹ F: -63.4
1-b	C: 47.4 (47.3) H: 2.0 (2.1) N: 4.6 (4.4)	¹ H: 6.4 (1H), 6.75 (1H), 7.7 (1H), 7.8 (1H), 7.95 (1H), 8.05 (1H) ¹⁹ F: -63.4 (s); -109.5 (ddd)
1-c	C: 47.4 (47.2) H: 2.0 (2.0) N: 4.6 (4.5)	¹ H: 6.6 (1H), 6.7 (1H), 6.9 (1H), 7.8 (1H), 8.0 (1H), 8.6 (1H) ¹⁹ F: -63.5 (s); -112.8 (ddd)
1-d	C: 55.9 (56.1) H: 3.0 (3.2) N: 5.9 (5.8)	¹ H: 6.6 (2H), 6.8 (1H), 7.0 (1H), 7.6 (1H), 7.7 (1H), 8.4 (1H) ¹⁹ F: -115.0 (ddd)
1-e	C: 44.1 (43.3) H: 1.7 (2.1) N: 3.9 (3.6)	¹ H: 6.9 (1H), 7.1 (1H), 7.8 (1H), 8.0 (2H), 8.2 (1H) ¹⁹ F: -63.0 (1F), -63.4 (1F)
1-f	C: 50.4 (50.5) H: 2.5 (2.7) N: 4.9 (4.9)	¹ H: 6.9 (1H), 7.1 (2H), 7.6 (1H), 7.8 (1H), 7.9 (1H), 8.1 (1H) ¹⁹ F: -62.4

TABLE 5 (continued)		
Compound	Analysis (calcd (found))	NMR (CD ₂ Cl ₂ , 25°C)
1-g	C: 55.9 (56.3) H: 3.0 (3.2) N: 5.9 (6.0)	¹ H: 6.4 (1H), 6.7 (1H), 7.0 (1H), 7.6 (1H), 7.7 (2H), 7.9 (1H) ¹⁹ F: -112.6 (ddd)
1-h	C: 51.0 (45.2) H: 2.1 (2.3) N: 4.9 (4.2)	¹ H: 6.8 (1H), 6.95 (1H), 7.05 (1H), 7.7 (1H), 8.0 (1H), 8.9 (1H) ¹⁹ F: -63.3
1-i	C: 49.4 (49.3) H: 2.9 (2.8) N: 4.4 (4.4)	¹ H: 3.6 (3H), 6.3 (1H), 6.6 (1H), 7.7 (2H), 7.85 (1H), 7.95 (1H) ¹⁹ F: -63.2
1-j	C: 47.4 (47.4) H: 2.0 (2.3) N: 4.6 (4.7)	¹ H: 6.7 (m), 7.1 (m), 7.5 (m), 7.6 (m), 7.7 (m), 8.0 (m), 8.2 (m) ¹⁹ F: 8 s resonances (-63.0 - -63.6) and 8 ddd resonances (-92.2 - -125.5)
1-k	C: 43.5 (44.0) H: 1.8 (2.1) N: 8.5 (8.4)	¹ H: 6.9 (1H), 7.15 (1H), 8.1 (1H), 8.3 (1H), 8.45 (1H), 8.6 (1H) ¹⁹ F: -62.9
1-l	C: 42.2 (42.1) H: 16. (1.8) N: 3.8 (3.7)	¹ H: 6.5 (1H), 6.7 (1H), 7.75 (1H), 7.85 (1H), 8.0 (1H), 8.1 (1H) ¹⁹ F: -58.1 (1F), -63.4 (1F)

EXAMPLE 3

This example illustrates the preparation of iridium complexes of the Second Formula $\text{IrL}^a\text{L}^b\text{L}^c\text{L}'_x\text{L}''_y\text{L}'''_z$ above,

Compound 1-n

- 5 A mixture of $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$ (54% Ir; 510 mg), 2-(3-trifluoromethylphenyl)-quinoline (1.80 g), and silver trifluoroacetate (1.10 g) was vigorously stirred at 190-195°C for 4 hours. The resulting solid was chromatographed on silica with dichloromethane to produce a mixture of the dicyclometalated complex and the unreacted ligand. The latter was removed from the mixture by extraction with
- 10 warm hexanes. After the extracts became colorless the hexane-insoluble solid was collected and dried under vacuum. The yield was 0.29 g. ^{19}F NMR: -63.5 (s, 6F), -76.5 (s, 3F). The structure of this complex was established by a single crystal X ray diffraction study.

Compound 1-o

- 15 A mixture of $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$ (54% Ir; 500 mg), 2-(2-fluorophenyl)-3-chloro-5-trifluoromethylpyridine (2.22 g), water (0.3 mL), and silver trifluoroacetate (1.00 g) was stirred at 190°C for 1.5 hours. The solid product was chromatographed on silica with dichloromethane to produce 0.33 g of a 2:1 co-crystallized adduct of the dicyclometalated aqua trifluoroacetato complex,
- 20 compound 1-p, and the unreacted ligand. ^{19}F NMR: -63.0 (9F), -76.5 (3F), -87.7 (2F), -114.4 (1F). The co-crystallized phenylpyridine ligand was removed by recrystallization from dichloromethane-hexanes. The structures of both the adduct and the complex were established by a single crystal X-ray diffraction study.

EXAMPLE 4

25 This example illustrates the preparation of an hydroxo iridium dimer, having structure (VIII) above.

- A mixture of $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$ (54% Ir; 510 mg), 2-(4-fluorophenyl)-5-trifluoromethylpyridine (725 mg), water (5 mL), and 2-ethoxyethanol (20 mL)
- 30 was vigorously stirred under reflux for 4.5 hours. After a solution of NaOH (2.3 g) in water (5 mL) was added, followed by 20 mL of water, the mixture was stirred under reflux for 2 hours. The mixture was cooled down to room temperature, diluted with 50 mL of water, and filtered. The solid was vigorously stirred under reflux with 30 mL of 1,2-dichloroethane and aqueous NaOH (2.2 g
- 35 in 8 mL of water) for 6 hours. The organic solvent was evaporated from the mixture to leave a suspension of an orange solid in the aqueous phase. The orange solid was separated by filtration, thoroughly washed with water, and dried under vacuum to produce 0.94 g (95%) of the iridium hydroxo dimer

(spectroscopically pure). ^1H NMR (CD_2Cl_2): -1.0 (s, 1H, IrOH), 5.5 (dd, 2H), 6.6 (dt, 2H), 7.7 (dd, 2H), 7.9 (dd, 2H), 8.0 (d, 2H), 9.1 (d, 2H). ^{19}F NMR (CD_2Cl_2): -62.5 (s, 3F), -109.0 (ddd, 1F).

EXAMPLE 5

5 This example illustrates the preparation of bis-cyclometalated complexes from an iridium dimer.

Compound 1-p

A mixture of the iridium hydroxo dimer (100 mg) from Example 4, ethyl acetoacetate (0.075 mL; 4-fold excess), and dichloromethane (4 mL) was stirred
10 at room temperature overnight. The solution was filtered through a short silica plug and evaporated to give an orange-yellow solid which was washed with hexanes and dried. The yield of the complex was 109 mg (94%). ^1H NMR (CD_2Cl_2): 1.1 (t, CH_3), 3.9 (dm, CH_2), 4.8 (s, CH_3COCH), 5.9 (m), 6.7 (m), 7.7 (m), 8.0 (m), 8.8 (d). ^{19}F NMR (CD_2Cl_2): -63.1 (s, 3F), -63.2 (s, 3F), -109.1
15 (ddd, 1F), -109.5 (ddd). Analysis: Calcd: C, 44.9; H, 2.6; N, 3.5. Found: C, 44.4; H, 2.6; N, 3.3.

Compound 1-w

A solution of hydroxo iridium dimer from Example 4 (0.20 g) in THF (6 mL) was treated with 50 mg of trifluoroacetic acid, filtered through a short
20 silica plug, evaporated to ca. 0.5 mL, treated with hexanes (8 mL), and left overnight. The yellow crystalline solid was separated, washed with hexanes, and dried under vacuum. Yield (1:1 THF solvate): 0.24 g (96%). ^{19}F NMR (CD_2Cl_2 , 20 °C), δ : -63.2 (s, 3F), -76.4 (s, 3F), -107.3 (ddd, 1F). ^1H NMR (CD_2Cl_2 , 20 °C), δ : 9.2 (br s, 1H), 8.2 (dd, 1H), 8.1 (d, 1H), 7.7 (m, 1H), 6.7 (m, 1H), 5.8 (dd, 1H),
25 3.7 (m, 2H, THF), 1.8 (m, 2H, THF).

Compound 1-x

A mixture of the trifluoroacetate intermediate, compound 1-w (75 mg), and 2-(4-bromophenyl)-5-bromopyridine (130 mg) was stirred under N_2 at 150-155 °C for 30 min. The resulting solid was cooled to room temperature and
30 dissolved in CH_2Cl_2 . The resulting solution was filtered through silica gel and evaporated. The residue was washed several times with warm hexanes and dried under vacuum to leave a yellow, yellow-photoluminescent solid. Yield: 74 mg (86%). ^{19}F NMR (CD_2Cl_2 , 20 °C), δ : -63.1 (s, 3F), -63.3 (s, 3F), -108.8 (ddd, 1F), -109.1 (ddd, 1F). ^1H NMR (CD_2Cl_2 , 20 °C), δ : 8.2 (s), 7.9 (m), 7.7 (m), 7.0 (d), 6.7 (m), 6.2 (dd), 6.0 (dd). The complex was meridional, with the nitrogens
35 of the fluorinated ligands being trans, as confirmed by X-ray analysis.

EXAMPLE 6

This example illustrates the preparation of iridium compounds of the Fifth Formula $mer\text{-Ir(L}^a)_3$ above.

Compound 1-s

- 5 This complex was synthesized in a manner similar to compound 1-n. According to the NMR, TLC, and TGA data, the result was an approximately 1:1 mixture of the facial and meridional isomers.

Compound 1-t

- 10 A mixture of $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$ (54% Ir; 0.40 g), 2-(3,5-difluorophenyl)-5-trifluoromethylpyridine (1.40 g), AgOCOCF_3 (0.81 g), and water (0.5 mL) was vigorously stirred under a flow of N_2 as the temperature was slowly (30-40 min) brought up to 165°C (oil bath). After 40 min at 165°C the mixture solidified. The mixture was cooled down to room temperature. The solids were extracted with dichloromethane until the extracts decolorized. The combined dichloromethane
- 15 solutions were filtered through a short silica column and evaporated. The residue was thoroughly washed with hexanes and dried under vacuum. Yield: 0.53 g (49%). ^{19}F NMR (CD_2Cl_2 , 20°C), δ : -63.55 (s, 3F), -63.57 (s, 3F), -63.67 (s, 3F), -89.1 (t, 1F), -100.6 (t, 1F), -102.8 (dd, 1F), -118.6 (ddd, 1F), -119.3 (ddd, 1F), -123.3 (ddd, 1F). ^1H NMR (CD_2Cl_2 , 20°C), δ : 8.4 (s), 8.1 (m), 7.9 (m), 7.6
- 20 (s), 7.5 (m), 6.6 (m), 6.4 (m). The complex was meridional, as was also confirmed by X-ray analysis.

Compound 1-u

- This complex was prepared and isolated similarly to compound 1-q, then purified by crystallization from 1,2-dichloroethane - hexanes. The yield of the
- 25 purified product was 53%. The complex is mer, as follows from the NMR data. ^{19}F NMR (CD_2Cl_2 , 20°C), δ : -63.48 (s, 3F), -63.52 (s, 6F), -105.5 (ddd, 1F), -105.9 (ddd, 1F), -106.1 (ddd, 1F), -107.4 (t, 1F), -107.9 (t, 1F), -109.3 (t, 1F). ^1H NMR (CD_2Cl_2 , 20°C), δ : 8.6 (m), 8.3 (s), 8.2 (s), 8.1 (m), 7.9 (m), 7.6 (m), 6.6 (m), 6.4 (m), 6.0 (m), 5.8 (m).

30 Compound 1-v

- This mer-complex was prepared in a manner similar to compound 1-w, using the trifluoroacetate dicyclometalated intermediate, compound 1-x, and 2-(4-fluorophenyl)-5-trifluoromethylpyridine. ^{19}F NMR (CD_2Cl_2 , 20°C), δ :
- 35 -63.30 (s, 3F), -63.34 (s, 3F), -63.37 (s, 3F), -108.9 (ddd, 1F), -109.0 (ddd, 1F), -109.7 (ddd, 1F). ^1H NMR (CD_2Cl_2 , 20°C), δ : 8.3-7.6 (m), 6.7 (m), 6.6 (dd), 6.3 (dd), 6.0 (dd). This yellow-luminescent meridional complex isomerised to the green luminescent facial isomer, compound 1-b, upon sublimation at 1 atm.

EXAMPLE 7

This example illustrates the formation of OLEDs using the iridium complexes of the invention.

Thin film OLED devices including a hole transport layer (HT layer),
5 electroluminescent layer (EL layer) and at least one electron transport layer (ET layer) were fabricated by the thermal evaporation technique. An Edward Auto 306 evaporator with oil diffusion pump was used. The base vacuum for all of the thin film deposition was in the range of 10^{-6} torr. The deposition chamber was capable of depositing five different films without the need to break up the
10 vacuum.

An indium tin oxide (ITO) coated glass substrate was used, having an ITO layer of about 1000-2000 Å. The substrate was first patterned by etching away the unwanted ITO area with 1N HCl solution, to form a first electrode pattern. Polyimide tape was used as the mask. The patterned ITO substrates were then
15 cleaned ultrasonically in aqueous detergent solution. The substrates were then rinsed with distilled water, followed by isopropanol, and then degreased in toluene vapor for ~3 hours.

The cleaned, patterned ITO substrate was then loaded into the vacuum chamber and the chamber was pumped down to 10^{-6} torr. The substrate was then
20 further cleaned using an oxygen plasma for about 5-10 minutes. After cleaning, multiple layers of thin films were then deposited sequentially onto the substrate by thermal evaporation. Finally, patterned metal electrodes of Al were deposited through a mask. The thickness of the film was measured during deposition using a quartz crystal monitor (Sycon STC-200). All film thickness reported in the
25 Examples are nominal, calculated assuming the density of the material deposited to be one. The completed OLED device was then taken out of the vacuum chamber and characterized immediately without encapsulation.

A summary of the device layers and thicknesses is given in Table 6. In all cases the anode was ITO as discussed above, and the cathode was Al having a
30 thickness in the range of 700-760 Å. In some of the samples, a two-layer electron transport layer was used. The layer indicated first was applied adjacent to the EL layer.

TABLE 6			
Alq_3 = tris(8-hydroxyquinolato) aluminum DDPA = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline Ir(ppy)_3 = fac-tris(2-phenylpyridine) iridium MPMP = bis[4-(N,N-diethylamino)-2-methylphenyl](4-methylphenyl)methane			
Sample	HT layer (Thickness, Å)	EL layer (Thickness, Å)	ET layer (Thickness, Å)
Comparative	MPMP (528)	Ir(ppy)_3 (408)	DDPA (106) + Alq_3 (320)
1	MPMP (520)	Compound <u>1-b</u> (499)	DDPA (125) + Alq_3 (365)
2	MPMP (541)	Compound <u>1-b</u> (580)	DDPA (407)
3	MPMP (540)	Compound <u>1-e</u> (499)	DDPA (112) + Alq_3 (340)
4	MPMP (525)	Compound <u>1-k</u> (406)	DDPA (106) Alq_3 (341)
5	MPMP (570)	Compound <u>1-i</u> (441)	DDPA (107) + Alq_3 (339)
6	MPMP (545)	Compound <u>1-j</u> (462)	DDPA (111) + Alq_3 (319)
7	MPMP (643)	Compound <u>1-g</u> (409)	DDPA (112) + Alq_3 (361)
8	MPMP (539)	Compound <u>1-f</u> (430)	DDPA (109) + Alq_3 (318)
9	MPMP (547)	Compound <u>1-a</u> (412)	DDPA (105) + Alq_3 (300)
10	MPMP (532)	Compound <u>1-h</u> (457)	DDPA (108) + Alq_3 (306)
11	MPMP (603)	Compound <u>1-d</u> (415)	DDPA (111) + Alq_3 (303)
12	MPMP (551)	Compound <u>1-c</u> (465)	DDPA (106) + Alq_3 (313)
13	MPMP (520)	Compound <u>1-l</u> (405)	DDPA (410)

TABLE 6 (continued)			
Sample	HT layer (Thickness, Å)	EL layer (Thickness, Å)	ET layer (Thickness, Å)
14	MPMP (504)	Compound <u>1-b</u> (400)	DDPA (393)
15	MPMP (518)	Compound <u>1-b</u> (153)	DDPA (418)
16	MPMP (556)	Compound <u>1-m</u> (416)	DDPA (430)
17	MPMP (520)	Compound <u>1-n</u> (419)	DDPA (420)
18	MPMP (511)	Compound <u>1-o</u> (412)	DDPA (413)
19	MPMP (527)	Compound <u>1-p</u> (425)	DDPA (412)
20	MPMP (504)	Compound 1-q (417)	DPA (407)
21	MPMP (525)	Compound 1-t (419)	DPA (416)
22	MPMP (520)	Compound 1-u (421)	DPA (405)

The OLED samples were characterized by measuring their (1) current-voltage (I-V) curves, (2) electroluminescence radiance versus voltage, and (3) electroluminescence spectra versus voltage. The apparatus used, 200, is shown in Figure 2. The I-V curves of an OLED sample, 220, were measured with a Keithley Source-Measurement Unit Model 237, 280. The electroluminescence radiance (in the unit of Cd/m^2) vs. voltage was measured with a Minolta LS-110 luminescence meter, 210, while the voltage was scanned using the Keithley SMU. The electroluminescence spectrum was obtained by collecting light using a pair of lenses, 230, through an electronic shutter, 240, dispersed through a spectrograph, 250, and then measured with a diode array detector, 260. All three measurements were performed at the same time and controlled by a computer, 270. The efficiency of the device at certain voltage is determined by dividing the electroluminescence radiance of the LED by the current density needed to run the device. The unit is in Cd/A .

The results are given in Table 7 below:

TABLE 7				
Electroluminescent Properties of Iridium Compounds				
Sample	Peak Radiance, Cd/m²	Efficiency at peak radiance, Cd/A	Peak efficiency, Cd/A	Approximate Peak Wavelengths, nm
Comparative	540 at 22 V	0.39	0.48	522
1	1400 at 21 V	3.4	11	525
2	1900 at 25 V	5.9	13	525
3	830 at 18 V	1.7	13.5	525
4	7.6 at 27 V	0.005	0.13	521
5	175 at 25 V	0.27	1.8	530, 563
6	514 at 20 V	1.5	2.2	560
7	800 at 26 V	0.57	1.9	514
8	1200 at 28 V	0.61	2	517
9	400 at 18 V	1.1	4	545
10	190 at 16 V	2.3	3.3	575
11	1150 at 25 V	1.2	3.8	506, 526
12	340 at 20 V	0.49	2.1	525
13	400 at 21 V	3	5	520
14	1900	5	9	525
15	2500	6	11	525
16	100 at 27 V	0.17	0.2	560
17	3.5 at 28 V	0.005	0.014	575
18	30 at 26 V	0.08	0.16	590

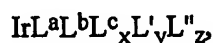
<u>TABLE 7</u> (continued)				
Sample	Peak Radiance, Cd/m ²	Efficiency at peak radiance, Cd/A	Peak efficiency, Cd/A	Approximate Peak Wavelengths, nm
19	2000 at 21 V	6	8	532
20	350 at 26 V	0.60	1.6	595
21	1200 at 22 V		5	545
22	80 at 19 V		1	540

The peak efficiency is the best indication of the value of the electroluminescent compound in a device. It gives a measure of how many electrons have to be input into a device in order to get a certain number of photons out (radiance). It is a fundamentally important number, which reflects the intrinsic efficiency of the light-emitting material. It is also important for practical applications, since higher efficiency means that fewer electrons are needed in order to achieve the same radiance, which in turn means lower power consumption. Higher efficiency devices also tend to have longer lifetimes, since a higher proportion of injected electrons are converted to photons, instead of generating heat or causing an undesirable chemical side reactions. Most of the iridium complexes of the invention have much higher peak efficiencies than the parent fac-tris(2-phenylpyridine) iridium complex. Those complexes with lower efficiencies may also find utility as phosphorescent or photoluminescent materials, or as catalysts, as discussed above.

CLAIMS

What is claimed is:

1. An organic electronic device comprising an emitting layer wherein at least 20% by weight of the emitting layer comprises at least one compound having a formula below:



where:

$x = 0$ or 1 , $y = 0$, 1 or 2 , and $z = 0$ or 1 , with the proviso that:

$x = 0$ or $y + z = 0$ and

when $y = 2$ then $z = 0$;

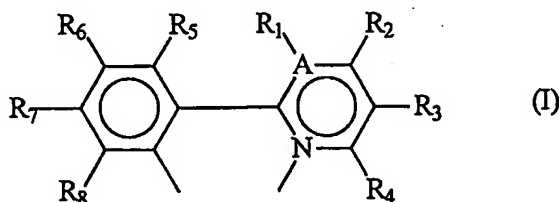
L' = a bidentate ligand or a monodentate ligand, and is not a phenylpyridine, phenylpyrimidine, or phenylquinoline; with the proviso that:

when L' is a monodentate ligand, $y+z = 2$, and

when L' is a bidentate ligand, $z = 0$;

L'' = a monodentate ligand, and is not a phenylpyridine, and phenylpyrimidine, or phenylquinoline; and

L^a , L^b and L^c are alike or different from each other and each of L^a , L^b and L^c has structure (I) below:



wherein:

adjacent pairs of $\text{R}_1\text{-R}_4$ and $\text{R}_5\text{-R}_8$ can be joined to form a five- or six-membered ring,

at least one of $\text{R}_1\text{-R}_8$ is selected from F , $\text{C}_n\text{F}_{2n+1}$,

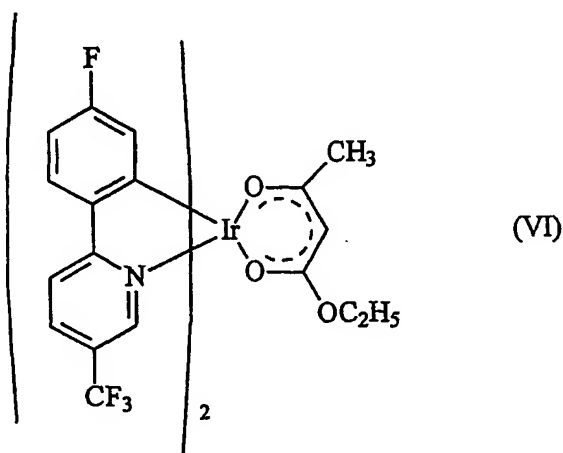
$\text{OC}_n\text{F}_{2n+1}$, and OCF_2X , where $n = 1\text{-}6$ and $\text{X} = \text{H}$, Cl , or Br , and

$\text{A} = \text{C}$ or N , provided that when $\text{A} = \text{N}$, there is no R_1 .

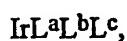
2. The device of Claim 1 wherein $x = 1$, $y = 0$, and $z = 0$.
3. The device of Claim 2 wherein $\text{A} = \text{C}$ and none of $\text{R}_1\text{-R}_8$ is selected from nitro.
4. The device of Claim 1 wherein R_3 is CF_3 .

5. The device of Claim 4 wherein at least one of R_5 - R_8 is selected from F , C_nF_{2n+1} , OC_nF_{2n+1} , and OCF_2X , where $n = 1-6$ and $X = H$, Cl , or Br .
6. The device of Claim 2 wherein $A = C$, $R_3 = CF_3$, $R_7 = F$, and R_1 , R_2 , R_4 - R_6 and $R_8 = H$.
7. The device of Claim 2 wherein $A = C$, R_3 and $R_6 = CF_3$, and R_1 , R_2 , R_4 , R_5 , R_7 and $R_8 = H$.
8. The device of Claim 2 wherein $A = C$, $R_3 = CF_3$, R_6 and $R_8 = F$, and R_1 , R_2 , R_4 , R_5 , and $R_7 = H$.
9. The device of Claim 1 wherein $x = 0$ and $y = 1$ having a structure (VI)

below:

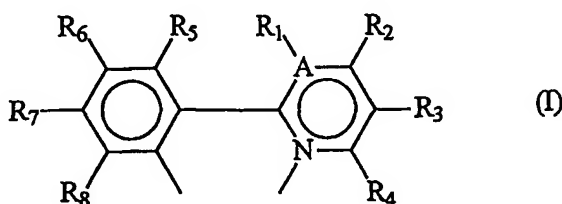


10. An organic electronic device comprising an emitting layer wherein the emitting layer comprises a diluent and less than 20% by weight of at least one compound that has a formula below:



where:

L^a , L^b and L^c are alike or different from each other and each of L^a , L^b and L^c has structure (I) below:



wherein:

adjacent pairs of R_1 - R_4 and R_5 - R_8 can be joined to form a five- or six-membered ring,

at least one of R_1 - R_8 is selected from F, C_nF_{2n+1} ,

5 OC_nF_{2n+1} , and OCF_2X , where $n = 1-6$ and $X = H, Cl, \text{ or } Br$, and

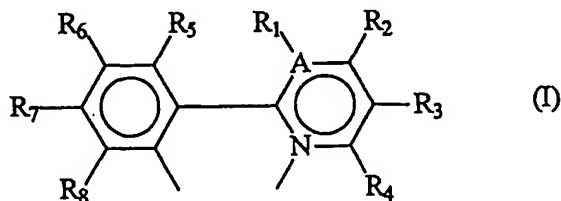
$A = C \text{ or } N$, provided that when $A = N$, there is no R_1 .

11. The device of Claim 10 wherein the diluent is selected from poly(N-vinyl carbazole), polysilane, 4,4'-N,N'-dicarbazole biphenyl, and tertiary aromatic amines.

10 12. The device of Claim 1, further comprising a hole transport layer selected from N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD), 1,1-bis[(di-4-tolylamino) phenyl]cyclohexane (TAPC), N,N'-bis(4-methylphenyl)-N,N'-bis(4-ethylphenyl)-[1,1'-(3,3'-dimethyl)biphenyl]-4,4'-diamine (ETPD), tetrakis-(3-methylphenyl)-N,N,N',N'-2,5-phenylenediamine (PDA),
15 -phenyl-4-N,N-diphenylaminostyrene (TPS), p-(diethylamino)-benzaldehyde diphenylhydrazone (DEH), triphenylamine (TPA), bis[4-(N,N-diethylamino)-2-methylphenyl](4-methylphenyl)methane (MPMP), 1-phenyl-3-[p-(diethylamino)styryl]-5-[p-(diethylamino)phenyl] pyrazoline (PPR or DEASP), 1,2-trans-bis(9H-carbazol-9-yl)cyclobutane (DCZB), N,N,N',N'-tetrakis(4-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TTB), porphyrinic compounds, and
20 combinations thereof.

13. The device of Claim 1, further comprising an electron transport layer selected from tris(8-hydroxyquinolato)aluminum, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (DDPA), 4,7-diphenyl-1,10-phenanthroline (DPA), 2-(4-biphenyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole (PBD), 3-(4-biphenyl)-4-phenyl-5-(4-t-butylphenyl)-1,2,4-triazole (TAZ), and combinations thereof.
25

14. A compound having a formula selected from *fac*-Ir(L)₃, *mer*-Ir(L)₃, and combinations thereof, where L is selected from group 1-a through 1-m and 1-q through 1-v, as shown in Table 1, and has structure (I) below:
30



wherein:

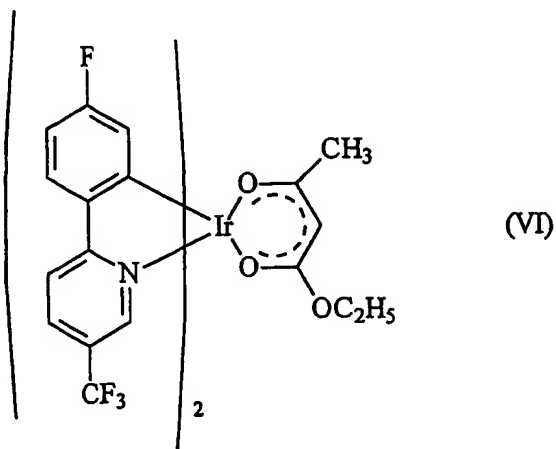
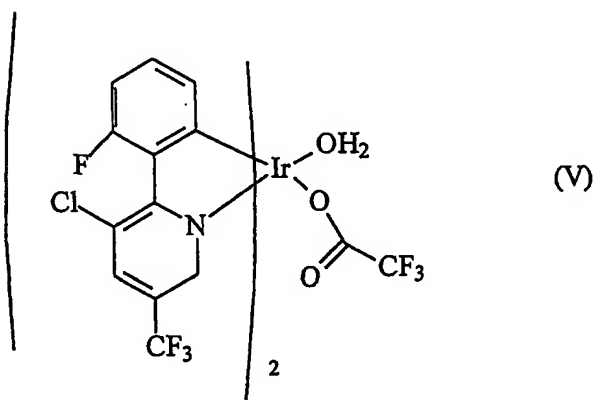
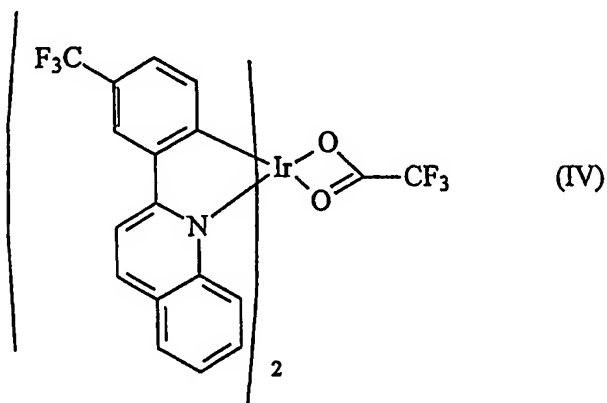
adjacent pairs of R_1 - R_4 and R_5 - R_8 can be joined to form a five- or six-membered ring,

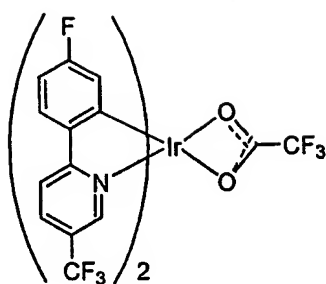
at least one of R_1 - R_8 is selected from F, C_nF_{2n+1} ,

OC_nF_{2n+1} , and OCF_2X , where $n = 1-6$ and $X = H, Cl, \text{ or } Br$, and

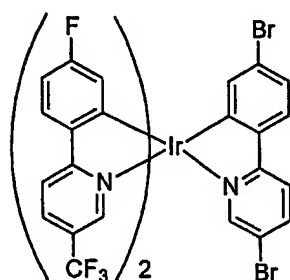
5 $A = C \text{ or } N$, provided that when $A = N$, there is no R_1 .

15. A compound having a structure selected from structures (IV), (V), (VI), (IX) and (X) below:





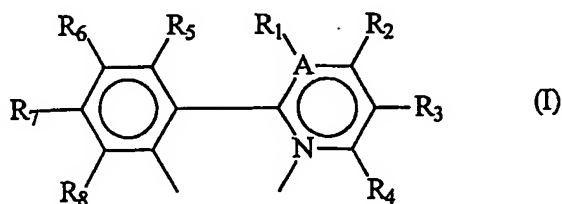
(IX)



(X)

16. An organic electronic device comprising an emitting layer that comprises a compound selected from the following (i) and (ii):

- (i) a compound having a formula selected from $fac-Ir(L)_3$, $mer-Ir(L)_3$, and combinations thereof, where L is a group selected from 1-a through 1-m and 1-q through 1-v, as shown in Table 1 and has structure (I) below:



(I)

wherein:

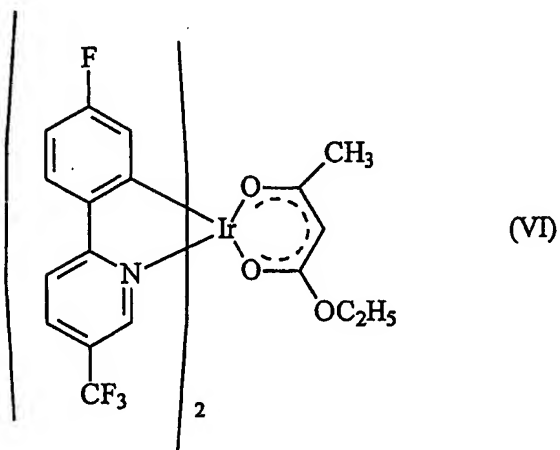
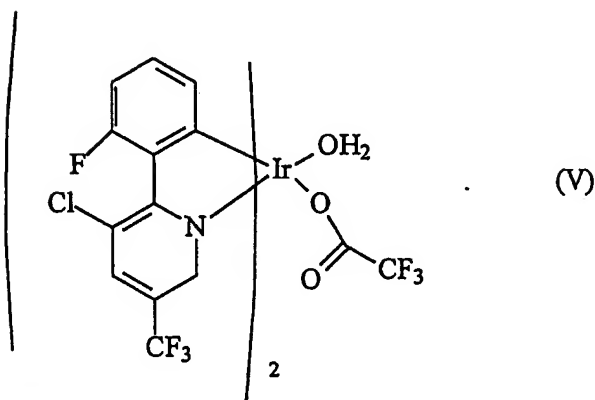
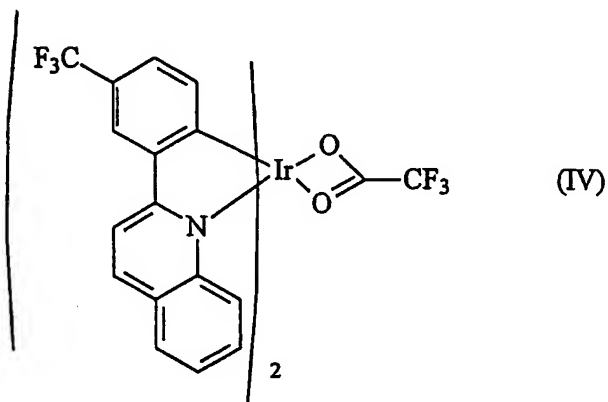
adjacent pairs of R_1-R_4 and R_5-R_8 can be joined to form a five- or six-membered ring,

at least one of R_1-R_8 is selected from F, C_nF_{2n+1} , OC_nF_{2n+1} , and OCF_2X , where $n = 1-6$ and $X = H, Cl, \text{ or } Br$, and

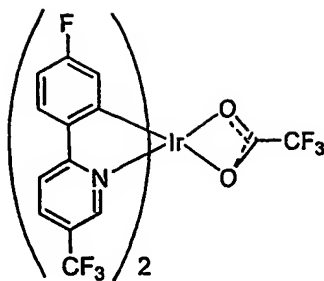
- A = C or N, provided that when A = N, there is no R₁;
 (ii) a compound having one of structures (IV), (V), (VI), (IX), and (X)

below:

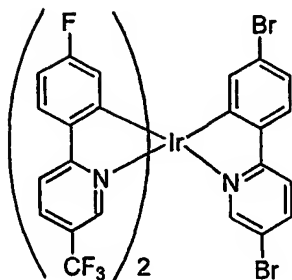
5



10



(IX)



(X)

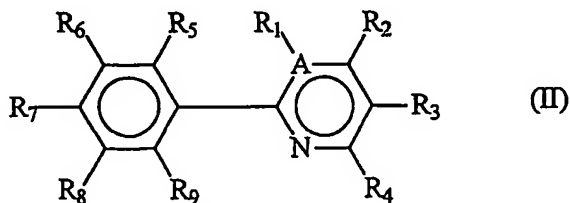
5

17. The device of Claim 16 wherein the emitting layer further comprises a diluent.

18. The device of Claim 17 wherein the diluent is selected from poly(N-vinyl carbazole), polysilane, 4,4'-N,N'-dicarbazole biphenyl, and tertiary aromatic amines.

10

19. A compound selected from compounds 2-a through 2-aa as shown in Table 2, having structure (II) below:



(II)

15

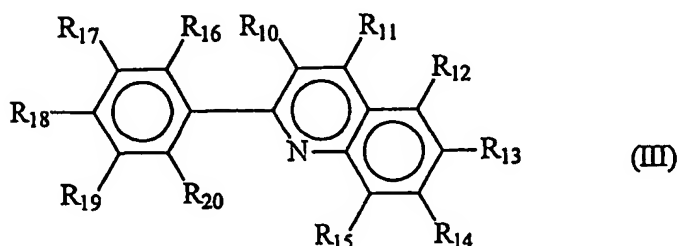
wherein: R_9 is H;

adjacent pairs of R_1 - R_4 and R_5 - R_8 can be joined to form a five- or six-membered ring;

at least one of R_1 - R_8 is selected from F, C_nF_{2n+1} ,
 OC_nF_{2n+1} , and OCF_2X , where $n = 1-6$ and $X = H, Cl, \text{ or } Br$, and
 $A = C \text{ or } N$, provided that when $A = N$, there is no R_1 .

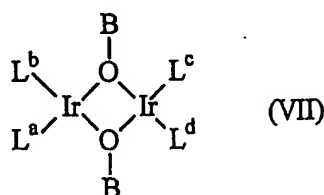
20. A compound having structure (III) below:

5



wherein $R_{17} = CF_3$ and R_{10} - R_{16} and R_{18} - $R_{20} = H$.

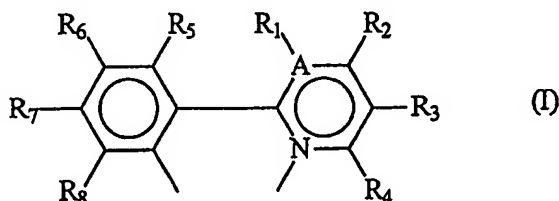
10 21. A compound having structure VII below:



wherein:

$B = H, CH_3, \text{ or } C_2H_5$;

15 $L^a, L^b, L^c, \text{ and } L^d$ are the same or different from each other; and
each of $L^a, L^b, L^c, \text{ and } L^d$ has structure (I) below:



20

wherein:

adjacent pairs of R_1 - R_4 and R_5 - R_8 can be joined to form a
five- or six-membered ring,

at least one of R_1 - R_8 is selected from F, C_nF_{2n+1} ,
 OC_nF_{2n+1} , and OCF_2X , where $n = 1-6$ and $X = H, Cl, \text{ or } Br$, and
 $A = C \text{ or } N$, provided that when $A = N$, there is no R_1 .

25

22. The compound of Claim 21 wherein:
- $L^a = L^b = L^c = L^d$;
- $B = H$;
- $R_3 = CF_3$;
- 5 $R_7 = F$;
- R_1, R_2, R_4-R_6 and $R_8 = H$.

1/1

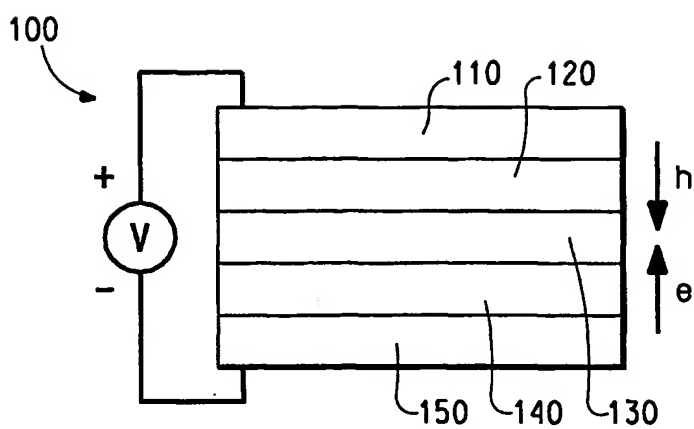


FIG. 1

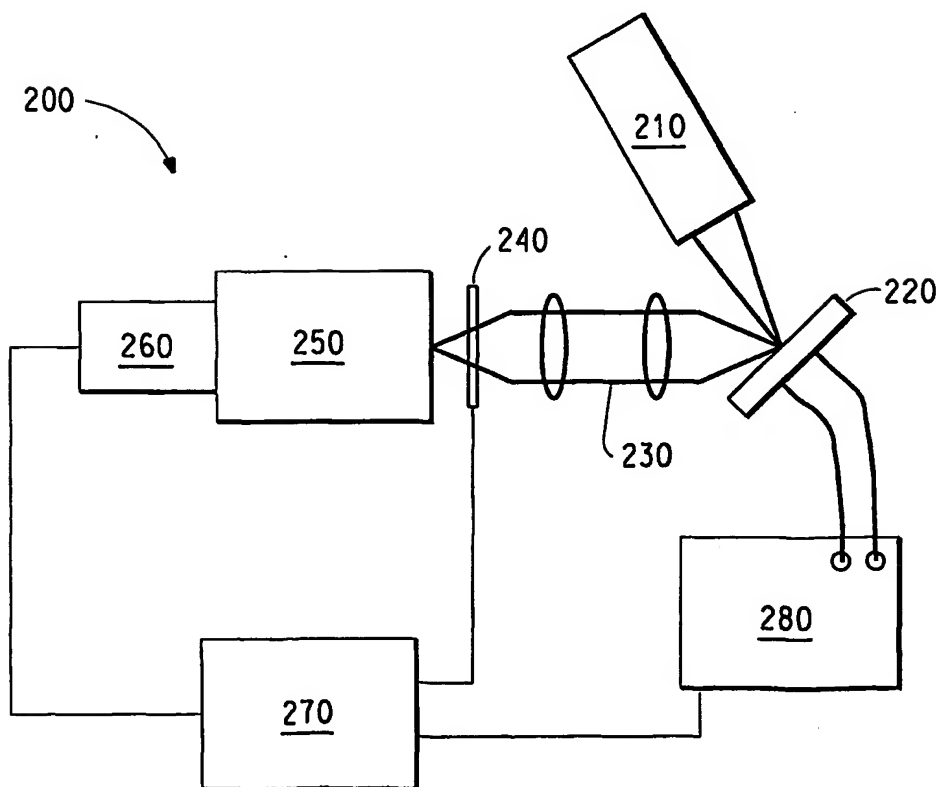


FIG. 2

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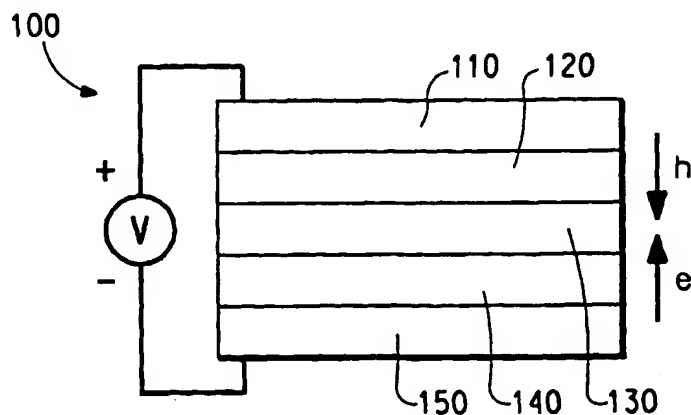
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ning of each regular issue of the PCT Gazette.*

(54) Title: **ELECTROLUMINESCENT IRIIDIUM COMPOUNDS WITH FLUORINATED PHENYLPYRIDINES,
PHENYLPYRIMIDINES, AND PHENYLQUINOLINES AND DEVICES MADE WITH SUCH COMPOUNDS**



(57) Abstract: The present invention is generally directed to electroluminescent Ir(III) compounds, the substituted 2-phenylpyridines, phenylpyrimidines, and phenylquinolines that are used to make the Ir(III) compounds, and devices that are made with the Ir(III) compounds.

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 01/20539

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H05B33/14 C09K11/06 H01L51/20 C07F15/00 C07D213/61
 C07D213/26 C07D213/68 C07D239/26 H01L51/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H05B C09K H01L C07F C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DJUROVICH PETER I ET AL: "Ir(III) CYCLOMETALATED COMPLEXES AS EFFICIENT PHOSPHORESCENT EMITTERS IN POLYMER BLEND AND ORGANIC LEDs" POLYMER PREPRINTS, vol. 41, no. 1, 2000 - March 2000 (2000-03), pages 770-771, XP001052648 cited in the application the whole document</p> <p style="text-align: center;">--- -/-</p>	1-3, 5, 10-13, 19

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

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O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/20539

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>CHATANI N; IE Y; KAKIUCHI F; MURAI S: "Ru₃(CO)₁₂-Catalyzed Reaction of Pyridylbenzenes with Carbon Monoxide and Olefins. Carbonylation at a C-H Bond in the Benzene Ring" JOURNAL OF ORGANIC CHEMISTRY, vol. 62, no. 8, 1997, pages 2604-2610, XP002201286 page 2606, column 2</p>	19
X	<p>GOSMINI C; NÉDÉLEC J Y; PÉRICHON J: "Electrosynthesis of functionalized 2-arylpyridines from functionalized aryl and pyridine halides catalyzed by nickel bromide 2,2'-bipyridine complex" TETRAHEDRON LETTERS, vol. 41, 2000 - 24 June 2000 (2000-06-24), pages 5039-5042, XP002201287 table 2</p>	19
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	-/--	

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/20539

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE CAPLUS 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; WANG, YUE ET AL: "(Hydroxyphenyl)pyridine derivative, its metal complexes and application a electroluminescence material" retrieved from STN Database accession no. 133:315395 XP002201289 abstract & CN 1 245 822 A (JILIN UNIV., PEOP. REP. CHINA) 1 March 2000 (2000-03-01)</p>	1-22
A	<p>DEDEIAN ET AL: "A NEW SYNTHETIC ROUTE TO THE PREPARATION OF A SERIES OF STRONG PHOTOREDUCING AGENTS: FAC TRIS-ORTHO-METALATED COMPLEXES OF IRIIDIUM (III) WITH SUBSTITUTED 2-PHENYLPYRIDINES" INORGANIC CHEMISTRY, AMERICAN CHEMICAL SOCIETY, EASTON, US, vol. 30, no. 30, 1991, pages 1685-1687, XP001070331 ISSN: 0020-1669 the whole document</p>	16,19

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 01/20539

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1 (part), 2, 3, 4(part), 5(part), 6-8, 10, 11, 12(part), 13(part), 14, 16-18(part)

Organic electronic device comprising an iridium complex IrLaLbLc (containing no other ligands L' or L'') as defined in claim 1.

- 1.1. Claims: 10, 11

Organic electronic device comprising an emitting layer and less than 20% by weight of at least one compound that has a formula IrLaLbLc as defined in claim 10.

- 1.2. Claims: 14, 16-18(part)

Compound having a formula selected from fac-Ir(L)_3 , mer-Ir(L)_3 , and combinations thereof as defined in claim 14 and organic electronic device comprising an emitting layer comprising this compound.

2. Claims: 1(part), 4(part), 5(part), 9, 12(part), 13(part), 15, 16-18(part)

Organic electronic device comprising an iridium complex IrLaLbL'L'' , $\text{IrLaLbL}'_2$, or ILaLbL' (containing no ligand Lc) as defined in claim 1.

3. Claim : 19

Organic ligand as defined in claim 19.

4. Claim : 20

Organic ligand as defined in claim 20.

5. Claims: 21-22

Iridium complex as defined in claim 21.

Please note that all inventions mentioned under item 1, although not necessarily linked by a common inventive concept, could be searched without effort justifying an additional fee.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/20539

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